Low Surface Energy Substrates Present Bonding Challenges

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Many plastics can be readily bonded with a wide range of adhesives to give strong structural bonds *(1)*. Plastics have much lower tensile strengths than other materials, such as metals, and adhesive bonds can be achieved that often exceed the strength of the plastic. However, attempts to bond certain plastics, such as polyethylene, result in weak assemblies. Weak assemblies include those with tensile shear strengths of less than 100 psi and those that readily fail under slight impact or exposure to moisture. The common characteristic of these unbondable plastics is low surface energy.

Typical low surface energy polymer substrates include plastics such as polyethylene and polypropylene, fluoroplastics like polytetrafluoroethylene (PTFE), polyolefin/rubber composites and thermoplastic olefins (TPOs). These polymers are of considerable interest to the design engineer because of their desirable properties, such as, for example, the chemical and heat resistance of PTFE and the low cost and easy moldability of polyolefins.

This report on structural bonding focuses on product assembly applications. It includes low stress situations where adhesives are used to hold parts together in noncritical situations and applications where there are considerable stresses on the bonded joints. Bonding of film, packaging and labeling applications are not included.

The polyolefins, polyethylene and polypropylene are of considerable commercial importance. For example, in the U.S. more than 80% of household plastics and more than 50% of toys are fabricated from these materials. There has also been a large increase in use of these plastics in the automotive industry. Polyolefins are relatively low cost thermoplastics that are easy to mold and have good mechanical properties coupled with good chemical resistance and excellent weather resistance. However, their use in many applications has been limited by the difficulty of assembling them in a cost effective way.

Polyolefins and fluoroplastics are difficult to bond for several reasons:

- Low surface energy. A prime requisite for successful adhesive bonding is successful spreading and wetting of the adhesive on the substrate. For this to be achieved, the substrate must have a high enough surface energy to overcome the surface tension forces in the adhesive. Polyolefins and fluoroplastics have very low surface energies.
- Low porosity. There is no opportunity for the adhesive to penetrate into the plastic and give mechanical interlocking.
- No functional groups. Polyolefins are comprised entirely of carbon and hydrogen atoms and are very nonpolar polymers. Most adhesives contain oxygen, nitrogen and other electron-rich atoms, and they are polar materials. Also, the carbon and hydrogen atoms in polyolefins are very unreactive toward many chemicals, thus precluding adhesion through chemical reactions.
- Surface weaknesses. Polyolefins usually have broad molecular weight distributions, and the low molecular weight molecules tend to migrate to the surface. These molecules have low tensile strengths and produce a weak boundary layer. Another common problem is the presence of mold release agents on the surface, which must be removed prior to adhesive bonding.

The following technologies represent the current state in the bonding of low energy polymer substrates.

Pretreatment

Thermal Methods. Flame treatment is widely used to prepare polyolefin surfaces for adhesive bonding, particularly in labeling operations. This method is purported to burn off contaminants and weak boundary layers, and it produces surface oxidation. Although flame treatment can be readily automated on a container labeling line, it is very impractical for most product assembly operations.

Polyolefins are thermoplastic polymers that can be easily melted, and several welding techniques can be utilized successfully to give strong bonds. These include spot welding, ultrasonic welding, ultrasonic staking, vibration welding, spin welding, hot plate welding and hot plate staking. All these methods can be successful, but often have severe limitations such as high capital requirements, restrictions on part geometry, inability to bond dissimilar materials or slow production cycles (often taking minutes per part compared to the seconds of adhesive bonding).

Chemical Surface Treatment. The chemical modification of low energy polymer surfaces is carried out by treatment with metallic sodium complex dispersions (for fluoroplastics), chromic acid etching, bleach/detergents, potassium iodate/sulfuric acid and other mixtures. Dutch authors *(2)* have shown that pretreatment with oxidizing acids can increase the adhesive strength of polyethylene tapes bonded with epoxy adhesives from 45 psi to 275 psi. Surface analysis of their treated specimens indicates the generation of functional oxygen containing groups, i.e., hydroxyl carbonyl and carboxyl. Similar work using chromosulfuric acid and chromyl chloride has been reported by Czech researchers *(3)*.

Treatment of PTFE with sodium complexes also gives strong evidence of surface oxidation and results in up to 10-fold increases in bond strength *(4)* with epoxy adhesives. Although bond strength can be improved significantly by these chemical methods, they are time-consuming batch processes, often taking hours to treat, wash and dry parts, and are thus only suitable for small, high value parts. There is also the problem of disposing of hazardous waste from these processes.

Comparison of Technologies for Bonding Low Surface Energy Polymers

Technology	Ultimate Bond Strength	Advantages	Disadvantages	Capital Costs	Cost Per Part	Potential for Future Development
Thermal Methods	High	Fast fixturing; no chemicals required	Only bonds simple parts; cannot bond dissimilar materials	High	Medium	Low
Chemical Surface Treatments	Medium	Universal for most plastics	Slow off-line batch process; hazardous chemicals involved	Medium	High	Low
Plasma Treatment	High	Universal for most plastics; clean process — no chemicals	Slow off-line batch process	High	High	Medium
Polymer Modification	Medium	Versatile — many different reactive groups can be introduced	Slow off-line batch process	High	High	Medium
Surface Primers	Very high — to the limit of the plastic	Simple process	Only for cyanoacrylates; volatile solvents in primer	Low	High	Low for cyanoacrylates; good for reactive acrylics
Hot Melt Adhesives	Medium	One-component adhesive; fast fixturing	Limited strengths; limited heat resistance	Medium	Low	Good

Plasma Treatment. Gas plasma treatment involves exposing the plastic to a gas activated by radio frequency energy to clean it and make it receptive to adhesives. Oxygen plasma treatment of polyethylene appears to remove weak boundary layers and oxidize the surface, leading to several-fold increases in bond strength with adhesives such as urethanes and epoxies.

Ammonia plasma treatment of polyethylene gives strong bonds with cyanoacrylate adhesives coupled with excellent strength retention upon water immersions *(5)*. It is argued that covalent bonding between the surface amine groups and the cyanoacrylate is more resistant to water than physical bonding alone.

Other Surface Treatments. The fluorination of polyolefins is a well-established batch process. German authors *(6)* have reported that fluorination of polypropylene and polyethylene gives a six fold increase in peel strength from 1.7 to 11.4 lb per linear inch when bonded to steel with a two-part epoxy adhesive. Evidence is presented that indicates covalent bond formation between the fluorinated surface and the amine component of the epoxy hardener. Other treatments that have been reported to enhance adhesion of polyolefins are contact with phosphorus trichloride in combination with UV radiation *(7)*, electrical discharge *(8)* and excimer laser treatment *(9)*.

Polymer Modification

Several attempts have been made to alter the surface or bulk properties of polyolefins to increase the surface energy or make them more polar. Several studies deal with grafting of polar monomers to the polyolefins. The photografting of methacrylic acid, acrylic acid, acrylamide and methacrylamide onto polyethylene indeed gave polymers an increase in tensile shear strength from 70 psi to 240 psi when tested with epoxy adhesives *(10)*, although a distinct trade-off was that the bond lines became hydrophilic and more susceptible to degradation by water. Other approaches have been to graft itaconic acid to polypropylene *(11)* acrylic acid to polyethylene after corona treatment *(12)*, maleic anhydride to polypropylene *(13)*, acrylamide to polypropylene after electrical discharge treatment *(14)*, and the bulk heterogeneous grafting of methyl methacrylate onto polypropylene powder *(15)*.

All these studies claim significant improvements in bond strength, often with failure of the plastic tested with epoxy adhesives. However, these procedures would, on a commercial scale, require considerable capital investment and use hazardous chemicals.

Surface Primers

All methods of pretreating or modifying low energy polymers prior to bonding are inconvenient, time consuming and often expensive. The use of a surface primer, although still somewhat inconvenient, is a much more desirable alternative for use on a production line.

The cyanoacrylate instant adhesives or superglues are widely used in product assembly operations because of their one-component nature, speed of cure and versatility. However, like most other adhesives, low strengths on untreated polyolefins has precluded their use in many operations. A significant breakthrough is the discovery by Loctite Corp. that certain surface primers can give considerable enhancements to adhesive strengths *(16)*. These primers are not used to pretreat the polyolefins; they are simply sprayed or brushed onto the substrate prior to applying the adhesive. All primers tested give increased bond strengths and the trialkylammonium carboxylates give bonds so strong that failure occurs in the polyolefin substrates (shear strengths of over 1,000 psi are consistently obtained).

Other companies have discovered primers that interact with cyanoacrylates *(17, 18)*. Henkel has patented the use of imidazole derivatives and claims that bond strengths increase with contact time with the substrate, prior to application of the adhesive.

Toa Gosei *(19)* has developed primers comprising solutions of imidazole compounds in combination with chlorinated polypropylene or methyl methacrylate/chloroprene copolymers. Koatsu Gas *(20)* has patented solutions of triethylphosphine and tri-N-propyl phosphine.

University researchers *(21)* have studied the interaction between solutions of two primers (triphenyl phosphine and cobalt actetylacetonate) and polyolefin surfaces in order to better understand why these primers promote adhesion using cyanoacrylates. These

primers produce bonds that exceed the strength of the plastics and also have good resistance to immersion in hot water. The dependence of adhesive performance on the solvent, primer thickness, age of the primed surface and the durability of the bond are explained by a model where the primer dissolves in the surface of the plastic and facilitates interpenetration of the cyanoacrylate. A significant finding in this work was that maximum performance is obtained when solvents for the primers are chosen that will both wet out on and swell the polyolefin.

Further credence is lent to this interpenetration theory when a similar effect is observed using a free radically cured acrylic adhesive system *(22)*. In this system, the primer consists of a solution of a copper(II) salt, and the adhesive is based on methyl methacrylate monomer with a small amount of trifunctional monomer and a hydroperoxide/amine-based cure system. It is found that bonds formed on low density polyethylene result in substrate failure, and that an interphase of mixed adhesive and polyethylene is formed up to 1.5 mm thick.

Hot Melt Adhesives

Hot melt adhesives are formulated using ethylene vinyl acetate (EVA) copolymers, polyamides, polyesters, thermoplastic rubbers and urethanes plus various additives to control flow, setting and adhesion. They have been used successfully to bond untreated polyolefins to themselves and to other materials. Hot melts are usually applied at temperatures of 350°F to 400°F. It has often been postulated that the molten hot melt dissolves surface contaminants and weak boundary layers, and can penetrate into the interior of the polyolefin substrate.

Evidence for the interpenetration theory to explain good bonding to polyolefins is shown as early as a 1976 study where hot melt EVA, ethyleneethyl acrylate and ethyleneacrylic acid copolymers were used to bond polyethylene *(23)*. Observation of cross sections of joints shows the existence of an interfacial boundary layer and a mixed layer of hot melt /polyethylene.

Russian authors *(24)* have studied the interaction of hot melt adhesives for bonding polyethylene to steel. They indicate that maximum adhesion is obtained when thermal oxidation leads to the crosslinking of the polyethylene. In addition, adhesion promoters for primerless polypropylene bonding with hot melts have been developed *(25)*. Effective formulations contain 33% isotactic polypropylene oligomers mixed with two types of styrene-butadiene-styrene block copolymers and two tackifiers. Lap shear strengths of 3.5 N/mm^2 are reported.

Adhesive shear strengths of 300 psi to 400 psi can be achieved with hot melts on bonding polypropylene and 200 psi to 300 psi on polyethylene. However, hot melts are often precluded from high-load-bearing situations because of their thermoplastic nature and low tensile strength compared to crosslinked adhesive types. They tend to creep under load, particularly at elevated temperatures. Hot melt compositions comprising blends of polyamides, EVA and hydrocarbon resins are purported to bond unpretreated polyethylene for such applications as cables and wires and to be durable under temperature variations between -20°F and 160°F *(26)*. It has also been claimed that moisture crosslinkable pressure sensitive hot melts can mitigate these weaknesses *(27)*.

Opportunities and Risks

Significant opportunities exist for structural adhesives that can bond untreated low energy substrates. Despite the worldwide increases in polyolefin prices over the last two years, prices will stabilize under normal cycles of supply/demand, and these plastics are still very desirable from both a cost and performance viewpoint.

Teltech believes that all types of pretreatment of the plastics will always be a last resort because of the inconvenience and cost of these treatments, and the necessity to pretreat will severely limit the potential for using polyolefin materials.

Cyanoacrylates, The discovery of surface primers for cyanoacrylate adhesives is a major technical breakthrough and will reap considerable profits for the marketers of these adhesives in specialized applications such as medical devices, electronics and sporting goods. However, we believe that both technical and economic constraints will limit the potential of this technology to these specialized and high-value-added applications.

Firstly, the use of a surface primer removes one of the main benefits of cyanoacrylates, namely, their single-component nature. Secondly, cyanoacrylates are thermoplastic adhesives with limited thermal and solvent resistance. Because properties are controlled primarily by the stability of the basic polymer backbone (almost all cyanoacrylates are based on ethyl cyanoacrylate monomer), there are limits to the property improvements that can be made. Thirdly, the high manufacturing cost of these adhesives coupled with the high profit expectations of their marketers will maintain most prices over $40/lb. This will eliminate cyanoacrylates from consideration in many large-area bonding applications.

Acrylics. The work on bonding polyolefins with acrylic adhesives has great potential. Acrylic adhesives are two-component, 100% reactive systems, often called tough acrylics, reactive acrylics or aerobic adhesives. They are based on methacrylate and acrylate monomers, which are toughened with dissolved rubbers. These adhesives have proven to be extremely useful in demanding applications where fixture times of a few minutes and strong, impact resistant bonds are required.

An attractive feature of acrylic adhesives is that with very few exceptions, they are formulated from commercially available monomers that are available at relatively low costs. However, acrylic adhesives have the inconvenience of being two-part systems, and some are flammable and have unpleasant odors. Nevertheless, the vast range of available raw materials makes them very attractive to the adhesives formulator. Also, single-component, heat-cured versions of these adhesives can be readily formulated.

Hot Melts. Hot melt adhesives have always had some successful applications in bonding polyolefins, a major reason being that they are compatible with polyolefins because many are formulated using polyolefin or ethylene-vinyl acetate polymers. Hot melts have failed in the past because of inability to withstand hot or cold temperatures during service or lack of resistance to creep under load. We believe that a combination of new resins and the increasing market penetration of moisture-curable crosslinking hot melts will remove some of these limitations.

Epoxies. It is interesting that there are no reported developments in the use of epoxy adhesives for bonding untreated low energy surfaces, although many researchers have used epoxies to test the efficacy of their surface treatments. Epoxy adhesives are widely used in industrial automotive and aerospace markets for the high-strength structural bonding of metals and composites. If the interpenetration theory is indeed one of the keys to successful polyolefin bonding, then a prime requirement for diffusion of the adhesive into the plastic will be a low viscosity. This is perhaps one of the reasons why epoxies have not been successful. The basic bisphenol A resins used in epoxies are 10,000 cps to 15,000 cps — compare this to the 5 cps to 20 cps of some of the cyanoacrylates and acrylic adhesives. The table on page 40 shows a comparison of the different approaches used to bond low surface energy materials.

Conclusion

Some significant advances have been made to address the problem of bonding low energy surfaces. The commercial availability of polyolefin primers for cyanoacrylates has certainly opened up new application opportunities for these adhesives, but the applications will be limited by high prices.

We believe that the academic work on the bonding of polyolefins with certain reactive acrylic adhesives is in its early stages, and it could lead to some exciting new products.

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